



# Effect of VC additive on MFA-based electrolyte in Li-ion batteries



Liwei Zhao, Shigeto Okada\*, Jun-ichi Yamaki

*Institute for Materials Chemistry and Engineering, Kyushu University, 6-1 Kasuga-Koen, Kasuga, Fukuoka 816-8580, Japan*

## HIGHLIGHTS

- ▶ VC was an effective SEI modification additive for MFA-based electrolyte.
- ▶ Higher VC concentration was needed at elevated temperature.
- ▶ At 60 °C, graphite in MFA + VC electrolyte showed outstanding cycling performance.
- ▶ MFA + VC electrolyte was a promising electrolyte for safer Li-ion batteries.

## ARTICLE INFO

### Article history:

Received 27 October 2012

Received in revised form

21 December 2012

Accepted 24 December 2012

Available online 17 January 2013

### Keywords:

Li-ion batteries

Electrolyte

Additive

Methyl difluoroacetate

Thermal stability

## ABSTRACT

Rapid capacity fading of a graphite electrode was obtained with LiPF<sub>6</sub>/MFA electrolyte due to poor properties of solid electrolyte interphase (SEI). Vinylene carbonate (VC) was therefore applied to the MFA-based electrolyte as an SEI modification additive. The effects of VC concentration on the electrochemical properties of the graphite/Li half-cell were investigated at 25 and 60 °C. At 25 °C, the graphite electrode in MFA + 1% VC-based electrolyte showed good capacity retention of 300 mA h g<sup>-1</sup> after 50 cycles, which was comparable with that in EC–DMC-based electrolyte; at 60 °C, the electrode in MFA + 3% VC-based electrolyte showed capacity retention of 240 mA h g<sup>-1</sup> after 50 cycles, which was much better than that in EC–DMC-based electrolyte. Overabundant VC additives showed negative effects because of the formation of too-thick and/or too-dense SEI. DSC measurements were carried out to study the thermal behavior of MFA-based electrolyte coexisting with lithiated graphite. VC-containing MFA-based electrolyte still showed much better thermal stability than EC–DMC-based electrolyte. TG–MS analysis was performed on delithiated graphite cycled in MFA-based electrolyte containing different VC concentrations to analyze VC's effect on SEI formation. In summary, VC-added MFA-based electrolyte was a promising electrolyte for the development of safer Li-ion batteries, especially at elevated temperature.

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

Rechargeable Li-ion batteries have been widely developed in various commercial fields, and seem to be excellent candidates for energy storage systems of electric vehicles and grid applications. However, the potential safety problems of Li-ion batteries become an obstacle to their practical application in large-scale batteries. With the scaling-up of batteries, the reduction of specific surface areas reduces the thermal dissipation rate. As heat accumulates in large-scale batteries, the thermal risk becomes much more serious than in normal batteries. Therefore, the control of heat generation becomes crucial to the design of safer batteries for large-scale devices.

Heat generation in a battery depends strongly on its components. Nowadays the most common electrolyte for Li-ion batteries is a solution of LiPF<sub>6</sub> salt dissolved in a mixture of alkyl carbonate solvents. The application of flammable organic solvent had been considered one of the primary reasons for the failure of the batteries in terms of safety. Many studies have been carried out about flame-retardant additives and co-solvents [1–3]. However, it was found recently that nonflammable organic electrolytes also could induce fire hazards of batteries [4]. Therefore, the most important characteristic for a safe battery electrolyte is good thermal stability at high temperature, instead of nonflammability.

Many of the fluorine-containing organic compounds have high thermal stability and quite unique properties. Some fluorinated organic solvents have been used as potential solvents or co-solvents for electrolytes [5–10]. Our group had dissolved LiPF<sub>6</sub> salt in several kinds of partially fluorinated carboxylic acid esters and obtained fluorinated ester electrolytes [11]. Among them,

\* Corresponding author. Tel./fax: +81 92 583 7841.

E-mail address: [s-okada@cm.kyushu-u.ac.jp](mailto:s-okada@cm.kyushu-u.ac.jp) (S. Okada).

methyl difluoroacetate ( $\text{CHF}_2\text{COOCH}_3$ , MFA)-based electrolyte showed the best electrochemical properties and the highest thermal stability coexisting with Li metal. Moreover,  $1 \text{ mol dm}^{-3}$   $\text{LiPF}_6$ /MFA electrolyte showed a higher ionic conductivity than commercial  $1 \text{ mol dm}^{-3}$   $\text{LiPF}_6$ /ethylene carbonate (EC)–dimethyl carbonate (DMC) electrolyte from  $-30$  to  $25^\circ\text{C}$  [12]. Therefore,  $1 \text{ mol dm}^{-3}$   $\text{LiPF}_6$ /MFA electrolyte was applied to carbon negative electrodes and the relative properties were investigated in detail [13]. Compared with commercial  $1 \text{ mol dm}^{-3}$   $\text{LiPF}_6$ /EC–DMC electrolyte, MFA-based electrolyte showed better thermal stability when it was mixed with lithiated carbon electrodes. However, due to the formation of a thick solid electrolyte interphase (SEI) on the carbon electrode surface, the reversible capacity obtained with MFA-based electrolyte was lower than that with the  $\text{LiPF}_6$ /EC–DMC electrolyte. This phenomenon became more serious in subsequent experiments. As partially fluorinated carboxylic acid ester had been reported to be rather unstable against the electrochemical reduction [5], the SEI formed with the  $\text{LiPF}_6$ /MFA electrolyte was suspected to have poor quality and to be unable to prevent a continuous reduction of MFA solvent during Li ion intercalation. Therefore, an SEI with a good passivation effect is necessary when MFA is applied as a bulk electrolyte solvent.

Vinylene carbonate (VC) is a highly strained cyclic alkyl carbonate with a polymerizable vinyl functionality [14]. Because of its high reduction potential of  $1.4 \text{ V}$  [15] vs.  $\text{Li/Li}^+$ , VC can be reduced to form an effective passivation film on the negative electrode surface before the bulk electrolyte components are involved [16]. Its marked effect on SEI modification had been demonstrated in many kinds of electrolyte [4,17–21]. It was reported that a small concentration of VC effectively improved the poor compatibility between the graphite electrode and propylene carbonate (PC)-based electrolyte [15,22]. In EC/linear carbonate-based electrolyte, VC also showed good properties, especially at elevated temperature [23–25].

Our group reported [26] that adding VC to  $\text{LiPF}_6$ /MFA electrolyte improved a cell's cycling performance greatly and showed little negative effect on the thermal stability of the  $\text{LiPF}_6$ /MFA electrolyte. To clarify the beneficial role of the VC additive on  $\text{LiPF}_6$ /MFA electrolyte, detailed studies on the effect of VC are still needed. In the present work, the effects of different concentrations of VC additives on the electrochemical properties of the MFA-based electrolyte were studied by charge/discharge measurements at  $25$  and  $60^\circ\text{C}$ . Moreover, a thermogravimetry–differential scanning calorimeter (TG–DSC) and a thermogravimetry–differential thermal analyzer combined with mass spectrometer (TG–DTA/MS) were used to study the thermal behavior of graphite electrode cycled in MFA/VC-based electrolyte at room and elevated temperatures. The effect of VC on SEI formation in MFA electrolyte was then investigated.

## 2. Experimental

MFA solvent (Daikin Fine Chemical Co. Ltd.) was used after being dehydrated by a molecular sieve  $3 \text{ \AA}$  1/8 in this work. When additive was needed for the electrolyte, 1, 3, and 5 vol.% VC (Mitsubishi Chemical) was added to the MFA solvent.  $\text{LiPF}_6$  salt was purchased from Stella Chemifa Corp.  $1 \text{ mol dm}^{-3}$   $\text{LiPF}_6$  electrolyte was prepared by dissolving  $\text{LiPF}_6$  salt in the MFA solvent or in the VC-added MFA solvent. The water content of the electrolyte was 30 ppm or less as estimated by the Karl Fischer method (CA100, Mitsubishi Chemical). For comparison, commercially available  $1 \text{ mol dm}^{-3}$   $\text{LiPF}_6$ /EC–DMC (1:1 vol., Tomiyama Chemicals) electrolyte was also used. To protect from oxygen and moisture, all samples were prepared in an Ar-filled glove box with a dew point below  $-70^\circ\text{C}$ .

Two-electrode half-cells (R2032) were used to evaluate the electrochemical properties of the electrolytes. Each cell consisted of a graphite working electrode, a polypropylene separator (Celgard

3501, Celgard LLC), and a lithium foil as a counter electrode. To make a slurry, 95 wt.% natural graphite (LF-18D, Chuetsu Graphite) and 5 wt.% polyvinylidene fluoride (PVdF) binder (KF#9100, Kureha Corp.) were dispersed in 1-methyl-2-pyrrolidinone (NMP). Working electrodes were prepared by spreading the slurry onto a 0.1-mm-thick porous Cu-foil current collector. Circular electrodes ( $15 \text{ mm}$  diameter) with a thickness of  $38\text{--}42 \text{ }\mu\text{m}$  and typical loading of  $6 \text{ mg cm}^{-2}$  active material were dried at  $120^\circ\text{C}$  for 12 h in a vacuum oven.

Electrochemical measurements were carried out in a constant temperature oven at  $25$  or  $60^\circ\text{C}$ . With MFA-based electrolytes, all cells were cycled between  $10$  and  $2000 \text{ mV}$  at a constant current density of  $0.2 \text{ mA cm}^{-2}$  (about  $0.1 \text{ C}$  rate), accompanied by 3 h of constant voltage charging at  $10 \text{ mV}$  during each cycle. For the cells with EC/DMC-based electrolyte, the constant voltage charging process was omitted. A relaxation period of 60 min followed each charge/discharge course for all cells. To get a delithiated graphite electrode, the cycling procedure was interrupted at a  $2000 \text{ mV}$  cutoff voltage after two cycles. To get a lithiated graphite electrode, the cycling procedure was interrupted at a  $10 \text{ mV}$  cutoff voltage after two cycles. All potentials reported in this work were referenced to the  $\text{Li/Li}^+$  redox couple.

For thermal analysis, the pre-cycled graphite/Li half-cell was disassembled in the Ar-filled glove box. The graphite electrode was rinsed and soaked in MFA or DMC solvent for 4 h and vacuum-dried at room temperature for 12 h. Most of the low-molecular-weight components were dissolved away from the electrode in the rinsing step and evacuated during vacuum drying. The electrode powder was then removed from the Cu current collector. For DSC analysis, the electrode powder was hermetically sealed in a stainless-steel pan together with some amount of correlative electrolyte. The temperature profile from room temperature to  $550^\circ\text{C}$  was obtained by a Thermo Plus TG–DSC 8230L system (Rigaku Corp.) at a heating rate of  $5^\circ\text{C min}^{-1}$ . During measurement, the TG signal was monitored simultaneously to confirm that the pan was hermetic. For TG–MS analysis, a Rigaku 8210H/5050AW TG–DTA/MS system was employed. Each sample was packed into a stainless steel pan and transferred into a TG chamber located in the glove box. As the temperature was increased to  $700^\circ\text{C}$  at a rate of

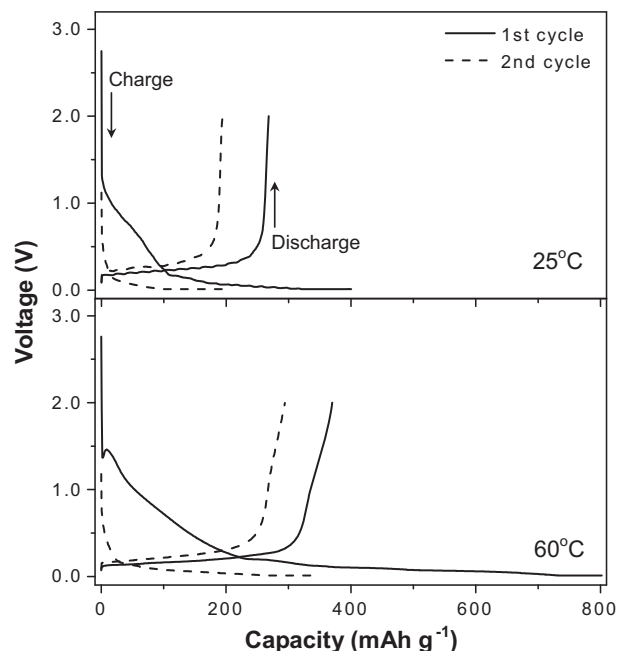


Fig. 1. The charge/discharge curves of graphite/Li half-cells with  $1 \text{ mol dm}^{-3}$   $\text{LiPF}_6$ /MFA electrolyte over the initial two cycles at different temperatures.

5 °C min<sup>-1</sup> under helium flow, the gaseous species released from the sample were monitored by MS.

### 3. Results and discussion

The electrochemical performance of MFA-based electrolyte was investigated before VC was added. Fig. 1 shows the charge/discharge curves of C/Li half-cells with 1 mol dm<sup>-3</sup> LiPF<sub>6</sub>/MFA over the initial two cycles at different temperatures. When the ambient temperature was set at 25 °C, the half-cell showed electrochemical behavior similar to that in our previous report [26]. A thick SEI was formed due to MFA decomposition and induced a large irreversible capacity of 130 mA h g<sup>-1</sup>. When the ambient temperature was set at 60 °C, the irreversible capacity increased sharply to 430 mA h g<sup>-1</sup>. In addition, a voltage reversion was observed at around 1.3 V during the first charge step. This indicated that a much thicker SEI was formed at elevated temperature, which drastically increased the interfacial resistance of graphite electrode and blocked Li ion transfer. This phenomenon also affected the cycling performance of the half-cells. For the cells at 25 °C, the cycling efficiency reached 96% in the second cycle. For the cells at 60 °C, however, 22 cycles were needed to arrive at the same value, which means a much slower increase in cycling efficiency. Obviously, at elevated temperature, the formation of stable SEI was prolonged to several tens of cycles, and a much thicker SEI was formed. Therefore, an SEI modification additive was necessary for MFA-based electrolyte, especially at elevated temperature.

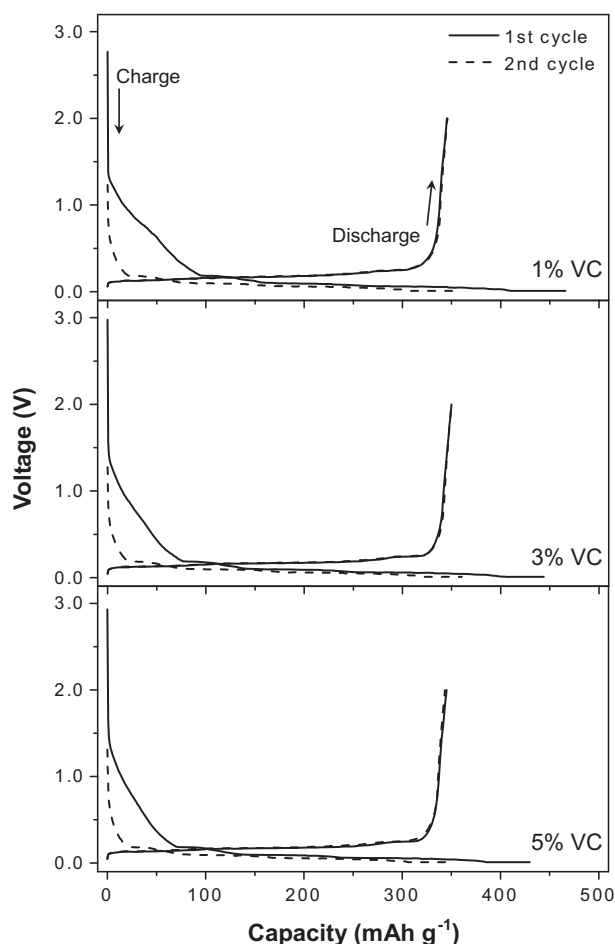


Fig. 2. The charge/discharge curves of graphite/Li half-cells with 1 mol dm<sup>-3</sup> LiPF<sub>6</sub>/MFA + VC electrolyte over the initial two cycles at 25 °C.

VC additives have been shown to improve the cycling performance of MFA-based electrolyte [26]. However, the effect of VC concentration on the improvement is still a question. Fig. 2 shows the variations of the charge/discharge curves of C/Li half-cells over the initial two cycles in relation to the VC concentration at 25 °C. In summary, the application of VC additives significantly decreased the irreversible capacity during the first cycle, so larger reversible capacity was obtained. Moreover, several voltage plateaus appeared in the curves regardless of the VC concentration, indicating that the SEI formed with VC additives had good Li ion conductivity, and that effective Li ion intercalation into graphite could be performed. On the other hand, the VC concentration also showed a direct effect on the charge/discharge behavior of the cells. When the VC concentration increased from 1% to 5%, the first charge capacity decreased from 466 to 430 mA h g<sup>-1</sup>, while the discharge capacity remained at about 345 mA h g<sup>-1</sup>. This means the irreversible capacity decreased with the VC concentration. In this respect, a higher VC concentration seems to be a better choice if cost is not a factor.

However, in the following cycles, the situation changed. Fig. 3 shows the cycling performance of the cells at 25 °C. For comparison, the data obtained with 1 mol dm<sup>-3</sup> LiPF<sub>6</sub>/MFA electrolyte and 1 mol dm<sup>-3</sup> LiPF<sub>6</sub>/EC–DMC electrolyte, respectively, are also presented. Obviously, capacity faded rapidly with 3% and 5% VC-added MFA electrolyte during prolonged cycling. After 50 cycles, only 134 and 89 mA h g<sup>-1</sup> discharge capacities were obtained with 3% VC–MFA and 5% VC–MFA electrolyte, respectively. In contrast, electrodes in MFA electrolyte with 1% VC showed good capacity retention of 300 mA h g<sup>-1</sup>, which was comparable with the 344 mA h g<sup>-1</sup> in EC–DMC-based electrolyte. Therefore, 1% VC was the best condition for cells working at 25 °C.

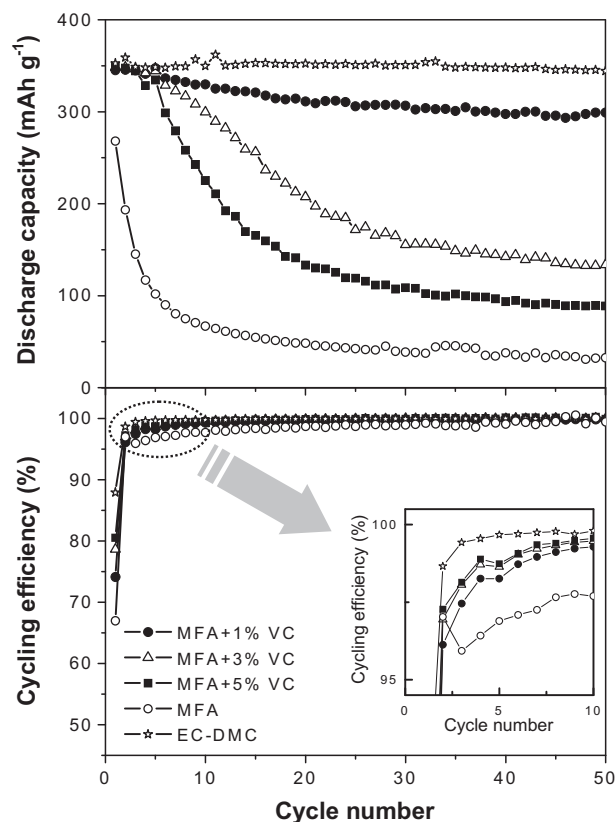


Fig. 3. The cycling performance of graphite/Li half-cells with 1 mol dm<sup>-3</sup> LiPF<sub>6</sub>/MFA + VC electrolyte at 25 °C.

When the ambient temperature increased to 60 °C, the effect of VC additives became more distinguished. Fig. 4 shows the variation of the charge/discharge curves of C/Li half-cells over the initial two cycles in relation to the VC concentration at 60 °C. With 1, 3, and 5% VC additives, the cells showed first irreversible capacities of 305, 210, and 150 mA h g<sup>-1</sup>, respectively, which were much lower than the 430 mA h g<sup>-1</sup> of MFA electrolyte with no VC additive. At the same time, the first discharge capacities were found to be about 365 mA h g<sup>-1</sup> regardless of the VC concentration. On the other hand, Li intercalation plateaus were also observed in the charge/discharge curves, as they were at 25 °C. In addition, the voltage-reversion phenomenon at around 1.3 V as shown in Fig. 1(b) was mitigated significantly with the increase in VC concentration. These phenomena indicated the formation of SEIs with good Li ion conductivity, especially under high VC concentration. However, compared with the cells at 25 °C, those at 60 °C showed much larger irreversible capacities. This difference was attributed to the formation of thicker SEI at elevated temperature.

As to the effect of VC concentration on cycling performance at 60 °C, it was found to be different from the situation at 25 °C. Fig. 5 shows the dependence of discharge capacity and cycling efficiency on cycle number for cells at 60 °C. Data obtained with MFA-based electrolyte and EC–DMC-based electrolyte, respectively, are also presented for comparison. In summary, cells with MFA + VC-based electrolytes showed much better capacity retention than those with EC–DMC-based electrolyte. After 50 cycles, the cells with MFA + 3% VC-based electrolyte maintained a reversible capacity of

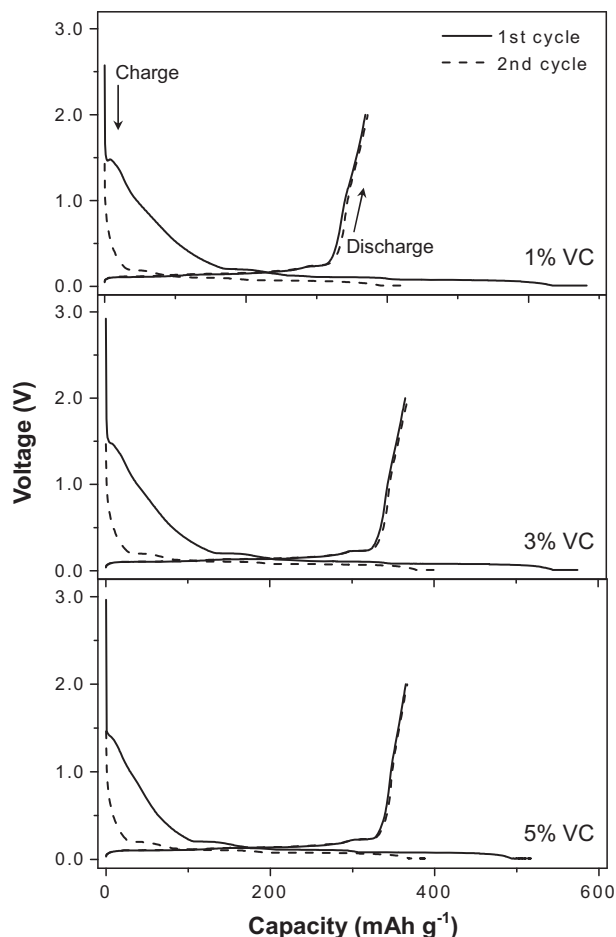


Fig. 4. The charge/discharge curves of graphite/Li half-cells with 1 mol dm<sup>-3</sup> LiPF<sub>6</sub>/MFA + VC electrolyte over the initial two cycles at 60 °C.

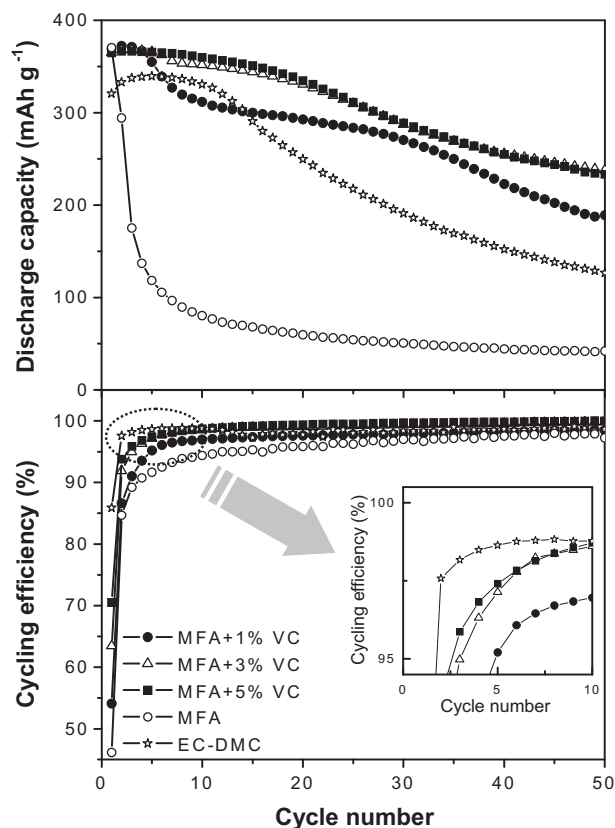


Fig. 5. The cycling performance of graphite/Li half-cells with 1 mol dm<sup>-3</sup> LiPF<sub>6</sub>/MFA + VC electrolyte at 60 °C.

238 mA h g<sup>-1</sup>, which was almost double the 126 mA h g<sup>-1</sup> of the cells with EC–DMC-based electrolyte. Nevertheless, the VC concentration in MFA-based electrolyte also directly affected cycling performance. Unlike that at 25 °C, MFA electrolytes with 3 and 5% VC additives showed rather comparable and good properties during prolonged cycling. It could be deduced from the tendency of the curves that 3% VC-added electrolyte might present a better capacity retention capability than the 5% VC-added one. In comparison, the electrolyte with 1% VC additives showed less capacity retention. This indicated that a higher VC concentration was needed for MFA-based electrolyte at elevated temperature.

Table 1 summarizes the discharge capacities of graphite electrodes after 50 cycles in different electrolytes and at different temperatures. The merit of the VC additives was distinguished, especially at elevated temperatures. However, although the merit of VC additives has been well reported and discussed, the negative effect of overabundant VC additives needs to be clarified. As discussed above, 1% VC was the best condition for MFA-based electrolyte at 25 °C, while 3% VC for that at 60 °C. However, from the insets of Figs. 3(b) and 5(b), it was clear that a higher VC

Table 1

Comparison of capacity retention of graphite electrodes after 50 cycles.

Electrolyte	Discharge capacity (mA h g <sup>-1</sup> )	
	25 °C	60 °C
1 mol dm <sup>-3</sup> LiPF <sub>6</sub> /MFA	33	42
1 mol dm <sup>-3</sup> LiPF <sub>6</sub> /MFA + 1% VC	300	189
1 mol dm <sup>-3</sup> LiPF <sub>6</sub> /MFA + 3% VC	134	240
1 mol dm <sup>-3</sup> LiPF <sub>6</sub> /MFA + 5% VC	89	233
1 mol dm <sup>-3</sup> LiPF <sub>6</sub> /EC–DMC (1:1 vol.)	344	127



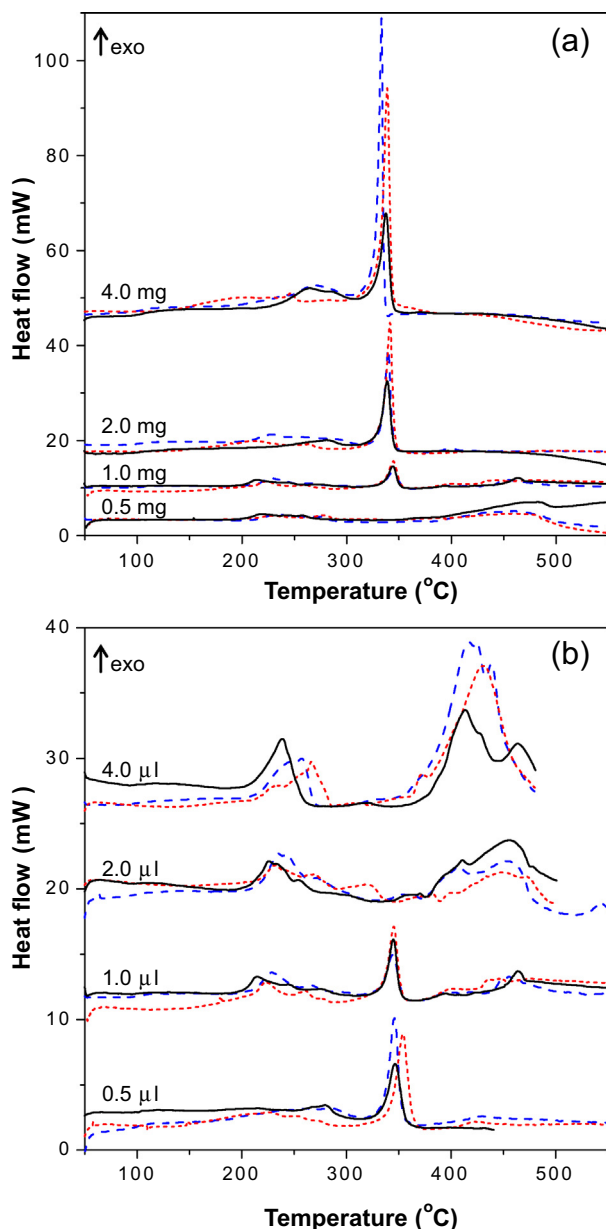
concentration induced a faster increase in cycling efficiency for the initial several cycles regardless of the ambient temperature. Normally, high cycling efficiency is accompanied by good capacity retention. Obviously we saw a counterexample here. High cycling efficiency meant effective SEI formation on the graphite electrode surface such that further electrolyte decomposition was prevented. So it could be deduced that, with higher VC concentration, thicker and/or denser SEI was formed because more VC was electrochemically decomposed. But when overabundant VC was used, the formed SEI became too thick and/or dense, and then the Li ion transfer through the SEI was blocked, thus inducing capacity fading. At elevated temperature, the penetration depth of solvent molecules increased, so thicker and/or denser SEI was needed. And the simultaneous increase in the transfer activity of Li ions overcame the SEI resistance barrier. This was the reason why the best VC

concentration for the electrolyte differed depending on the working temperature.

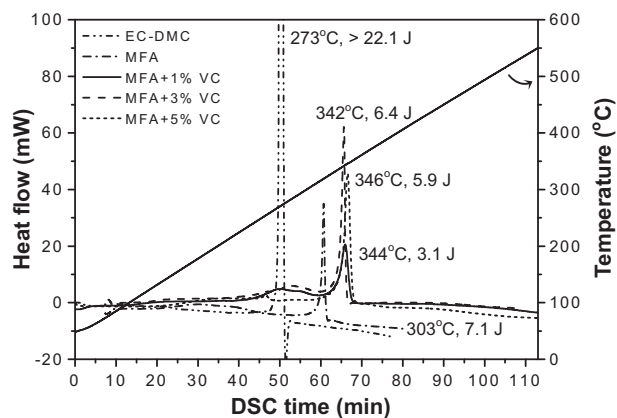
As an MFA-based electrolyte was introduced as a kind of thermally stable electrolyte, the effects of organic additives on the thermal stability of the electrolyte were of concern for its practical application. Therefore, DSC measurements were carried out to study the thermal behavior of the electrolytes coexisting with lithiated electrodes. Fig. 6 compares the DSC curves of the mixture of lithiated graphite and MFA-based electrolyte with 1, 3, and 5% VC additives. Two series comparisons were carried out. One was to increase the amount of electrode from 0.5 to 4.0 mg while the coexisting electrolyte was fixed at 1  $\mu\text{l}$ . The other was to increase the amount of electrolyte from 0.5 to 4.0  $\mu\text{l}$  while the coexisting electrode was fixed at 1 mg. In both series data, when the amounts of coexisting electrode and electrolyte were the same, the DSC curves for the mixtures showed high similarity regardless of the VC concentration in the electrolyte. This indicated that the thermal reactions in the mixture at elevated temperature were slightly affected by the VC concentration in the electrolyte. On the other hand, the exothermic peak intensities in the DSC curves were found to have some relationship with the VC concentration. A higher VC concentration could cause larger heat generation, especially when the lithiated graphite or electrolyte was overabundant.

To evaluate the thermal stability of MFA-based electrolyte, the DSC curves for mixtures of lithiated graphite electrodes with MFA-based electrolytes and 1 mol  $\text{dm}^{-3}$  LiPF<sub>6</sub>/EC–DMC electrolyte are compared as shown in Fig. 7. It was known from Fig. 6 that the thermal behavior of the mixture containing overabundant electrode was sensitive to the electrolyte component. Therefore, for the MFA-based electrolyte, a mixture of 4.0 mg lithiated graphite and 1  $\mu\text{l}$  electrolyte was selected for comparison. Except for the EC–DMC-based electrolyte, due to a drastic exothermic heat generation, only 2.5 mg lithiated graphite was mixed with 1  $\mu\text{l}$  electrolyte. Despite this, the mixture containing 1 mol  $\text{dm}^{-3}$  LiPF<sub>6</sub>/EC–DMC electrolyte showed much more heat generation and lower onset temperature than the mixtures containing MFA-based electrolytes with or without VC additives. So it was clear that MFA-based electrolyte has much better thermal stability than EC–DMC-based electrolyte. Considering the similar thermal stability for alkyl carbonate-based electrolytes, MFA + VC-based electrolyte is a potential substitute for the existing electrolyte.

To investigate the effect of VC concentration on the SEI component, TG–MS measurements were carried out on the delithiated electrodes after two cycles. For all delithiated graphite electrodes cycled in MFA electrolyte with different VC concentrations, CO<sub>2</sub> and CO were found to be the main components of gas species during



**Fig. 6.** DSC curves of a mixture of lithiated graphite and VC-containing MFA-based electrolyte: (a) is the DSC curves of a mixture of 1  $\mu\text{l}$  electrolyte and 0.5, 1, 2, and 4 mg electrode; (b) is the DSC curves of a mixture of 1 mg electrode and 0.5, 1, 2, and 4  $\mu\text{l}$  electrolyte. Solid lines are for 1% VC, dashed lines for 3% VC, and short dashed lines for 5% VC.



**Fig. 7.** Comparison of the heat generation from the mixtures of lithiated graphite and different electrolytes.

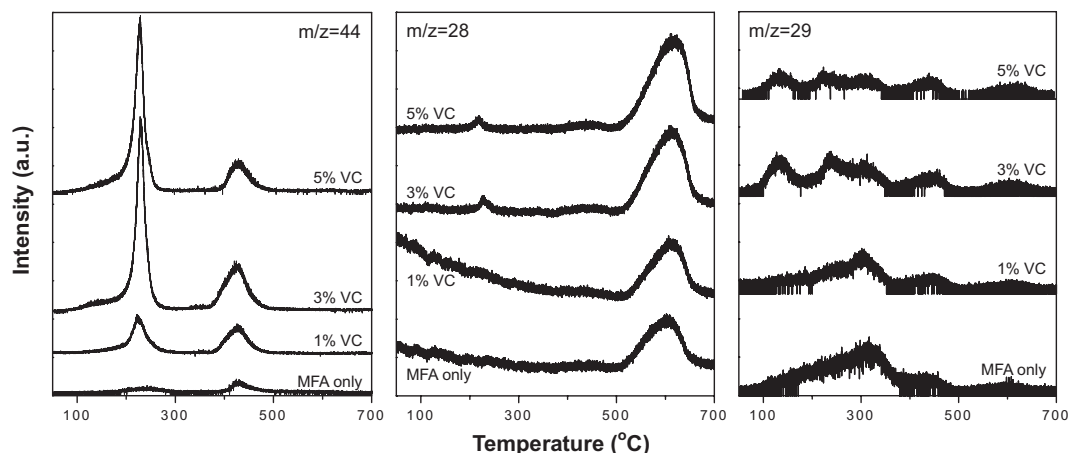


Fig. 8. Variation of the mass signals from SEI formed with different VC concentration in MFA-based electrolyte.

TG–MS analysis. Besides, a functional group  $-\text{CHO}$  was also found to be sensitive to VC concentration. No fluorine-contained gas species were detected. Fig. 8 shows the  $m/z = 44$ , 28, and 29 mass signals for the delithiated graphite electrode powder obtained with different VC concentrations. The results were related mainly to  $\text{CO}_2$ ,  $\text{CO}$ , and  $-\text{CHO}$ , respectively. For the signal of  $m/z = 44$ , two peaks were detected, at 230 and 425 °C. As increased with VC concentration rapidly, the former peak might be attributed to the VC reduction products, such as  $-\text{OCO}_2\text{Li}$ -containing polymeric component [24], because of the preferential reduction of VC before MFA during SEI formation [15]. In contrast, the peak at 425 °C showed rather constant intensity regardless of VC concentration, so the MFA reduction product was thought to contribute to this peak, such as  $\text{CHF}_2\text{COOLi}$  [13] or its possible further reduction product,  $\text{Li}_2\text{C}_2\text{O}_4$  [27]. As to the  $\text{CO}$  signal, because it appeared at more than 600 °C, it should be attributed to a final decomposition of all SEI components. On the other hand, the signal of  $m/z = 29$  was distributed in a wide temperature range and showed sensitivity to VC concentration, so it might be utilized as an SEI component sensor. Although the mechanism underlying each  $-\text{CHO}$  peak was not clarified, it was clear that the SEIs formed with 3 and 5% had quite similar components. This hypothesis is supported by the  $\text{CO}_2$  and  $\text{CO}$  signals.

#### 4. Conclusion

A  $\text{LiPF}_6/\text{MFA}$  solution has been studied as a potential candidate for safer electrolyte for Li-ion batteries. Half-cells with natural graphite as working electrodes were used to study the electrochemical characteristics of the MFA-based electrolyte. Because of the poor properties of the SEI that formed on the negative electrodes, the cells with  $\text{LiPF}_6/\text{MFA}$  electrolyte with no additives showed very large irreversible capacity and poor cycling performance, especially at elevated temperature. So 1, 3, and 5 vol.% VC was applied as SEI modification additive in the electrolyte. The effects of VC concentration on the electrochemical properties of graphite/Li half-cell were investigated at 25 and 60 °C. At 25 °C, the graphite electrode in MFA + 1% VC-based electrolyte showed good capacity retention of 300 mA h  $\text{g}^{-1}$  after 50 cycles, which was comparable with that in EC–DMC-based electrolyte; at 60 °C, the electrode in MFA + 3% VC-based electrolyte showed capacity retention of 240 mA h  $\text{g}^{-1}$  after 50 cycles, which was much better than that in EC–DMC-based electrolyte. On the other hand, overabundant VC additives showed a negative effect on the cells because of the formation of too-thick and/or too-dense SEI. DSC measurements were carried out to study the thermal behavior of

MFA-based electrolyte coexisting with lithiated graphite. VC-containing MFA-based electrolyte still showed much better thermal stability than EC–DMC-based electrolyte, although an increase in exothermic heat was observed with the increase in VC concentration. To discuss the effect of VC on SEI formation, TG–MS analysis was performed on delithiated graphite cycled in MFA-based electrolyte containing different VC concentrations. The SEIs formed with 3 and 5% VC showed similar components. In summary, VC-added MFA-based electrolyte is a promising candidate for the development of safer Li-ion batteries, especially at elevated temperature.

#### References

- [1] K. Kim, S. Ann, H.S. Kim, H.K. Liu, *Electrochim. Acta* 54 (2009) 2259.
- [2] S.V. Sazhin, M.K. Harrup, K.L. Gering, *J. Power Sources* 196 (2011) 3433.
- [3] K. Xu, *Chem. Rev.* 104 (2004) 4303.
- [4] Y. Shigematsu, M. Ue, J. Yamaki, *J. Electrochem. Soc.* 156 (2009) A176.
- [5] T. Nakajima, K. Dan, M. Koh, *J. Fluorine Chem.* 87 (1998) 221.
- [6] R. McMillan, H. Sleg, Z.X. Shu, W. Wang, *J. Power Sources* 81–82 (1999) 20.
- [7] J.O. Besenhard, W.K. Appel, L.H. Lie, G.H. Wrodnigg, K.-C. Moeller, M. Winter, in: Abstracts of the Second Hawaii Battery Conference, Hawaii, Hawaii Natural Energy Institute, and the University of Hawaii, Jan 4–7, 1999, p. 181.
- [8] T. Fujieda, *Kogyo Gijutsu* 41 (2000) 21.
- [9] K. Sato, I. Yamazaki, S. Okada, J. Yamaki, *Solid State Ionics* 148 (2002) 463.
- [10] R. Chandrasekaran, M. Koh, Y. Ozhawa, H. Aoyama, T. Nakajima, *J. Chem. Soc.* 121 (2009) 339.
- [11] J. Yamaki, I. Yamazaki, M. Egashira, S. Okada, *J. Power Sources* 102 (2001) 288.
- [12] T. Tanaka, T. Doi, S. Okada, J. Yamaki, *Fuel Cells* 9 (2009) 269.
- [13] M. Ihara, B.T. Hang, K. Sato, M. Egashira, S. Okada, J. Yamaki, *J. Electrochem. Soc.* 150 (2003) A1476.
- [14] C. Jehoulet, P. Biensan, J.M. Bodet, M. Broussely, C. Moteau, C. Tessier-Lescourret, in: *Proc. Electrochem. Soc.* 97–18 (Batteries for Portable Application and Electric Vehicles), The Electrochem. Soc. Inc., Pennington, NJ, 1997, p. 974.
- [15] X. Zhang, R. Kostecki, T.J. Richardson, J.K. Pugh, P.N. Ross Jr., *J. Electrochem. Soc.* 148 (2001) A1341.
- [16] S.S. Zhang, K. Xu, T.R. Jow, *Electrochim. Acta* 51 (2006) 1636.
- [17] M. Contestabile, M. Morselli, R. Paraventi, R.J. Neat, *J. Power Sources* 119–121 (2003) 943.
- [18] S. Herreyre, O. Huchet, S. Barusseau, F. Pertion, J.M. Bodet, Ph. Biensan, *J. Power Sources* 97–98 (2001) 576.
- [19] M. Broussely, P. Blanchard, Ph. Biensan, J.P. Planchat, K. Nechev, R.J. Staniewicz, *J. Power Sources* 119–121 (2003) 859.
- [20] M. Broussely, S. Herreyre, P. Biensan, P. Kasztajna, K. Nechev, R.J. Staniewicz, *J. Power Sources* 97–98 (2001) 13.
- [21] M. Fujimoto, Y. Shouji, T. Nohma, K. Nishio, *Denki Kagaku* 65 (1997) 949.
- [22] S.-K. Jeong, M. Inaba, R. Mogi, Y. Iriyama, Z. Ogumi, *Langmuir* 17 (2001) 8281.
- [23] J.C. Burns, N.N. Sinha, D.J. Coyle, G. Jain, C.M. VanElzen, W.M. Lamanna, A. Xiao, E. Scott, J.P. Gardner, J.R. Dahn, *J. Electrochem. Soc.* 159 (2012) A85.
- [24] D. Aurbach, K. Gamolsky, B. Markovsky, Y. Gofer, M. Schmidt, U. Heider, *Electrochim. Acta* 47 (2002) 1423.
- [25] M. Inaba, H. Tomiyasu, A. Tasaka, S.-K. Jeong, Z. Ogumi, *Langmuir* 20 (2004) 1348.
- [26] K. Sato, L. Zhao, S. Okada, J. Yamaki, *J. Power Sources* 196 (2011) 5617.
- [27] L. Zhao, I. Watanabe, T. Doi, S. Okada, J. Yamaki, *J. Power Sources* 161 (2006) 1275.